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14. ABSTRACT

An essential need of the US Air Force is the discovery, development, and fielding of new, energetic materials for advanced chemical propulsion in space and missile applications. Some of the key factors driving the requirement for new chemical propellants include: (a) improved performance in terms of increased specific impulse and density, (b) reduced sensitivity to external stimuli such as impact, friction, shock, and electrostatic discharge, and (c) mitigation of environmental and toxicological hazards (and the resulting costs) associated with currently used propellants.

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Design of Energetic Ionic Liquids (Preprint)

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An essential need of the US Air Force is the discovery, development, and fielding of new, energetic materials for advanced chemical propulsion in space and missile applications. Some of the key factors driving the requirement for new chemical propellants include: (a) improved performance in terms of increased specific impulse and density, (b) reduced sensitivity to external stimuli such as impact, friction, shock, and electrostatic discharge, and (c) mitigation of environmental and toxicological hazards (and the resulting costs) associated with currently used propellants.

A class of compounds which can potentially meet these requirements is known as ionic liquids (ILs), which are organic salts with unusually low melting points and vapor pressures. The physical and chemical properties of ILs render them useful for many purposes, most notably as environmentally benign ("green") solvents/reaction media but also as catalysts, electrolytes, etc.[1] From a Department of Defense (DoD) perspective, ILs are being explored as new propellants, explosives, and munitions. The Air Force in particular is interested in ILs for multiple propulsion applications, including their use as monopropellants, bipropellants, and working fluids for electric propulsion.[2] Some of the advantages of ILs relative to current propellant ingredients include increased density, higher specific impulse, reduced sensitivity, and lower toxicity. Furthermore, the properties of ILs can be carefully tuned, for example, via the choice of the component ions.

The overall objective of the Design of Energetic Ionic Liquids challenge project is to address several key technical issues and challenges associated with the characterization, design, and development of ILs as new propellant ingredients. Among these, for example, are a fundamental understanding of the (in)stability of ILs, the intrinsic nature of the short- and long-range structure and interactions between the component ions[2e-f], and identification of the key steps in the initial stages of decomposition and combustion[2a-c]. The research described in this article, which is a subset of the overall challenge project effort, is focused on the characterization of the structures, stabilities, and vibrational spectra of the gas-phase ion clusters of the 1-ethyl-3-methylimidazolium *bis*(trifluoromethyl)sulfonylimide ionic liquid, which has been selected as the propellant for the high-precision positioning demonstration.[3] In order to assess and tune the performance of these types of working fluids, it is necessary to characterize the exhaust plume, which contains a distribution of clusters, including $[Emim^+]_j[Im^-]_k$ ($j=k\pm1$); i.e., clusters containing either an excess cation or anion. The results of these calculations serve four main purposes: (1) to calculate the internal energy distribution functions of the ion clusters, which in turn are used to assess their thermal stability and to characterize the relative ion cluster populations, (2) to determine whether or not charge neutralization occurs in the ion clusters, (3) to provide a comparison between DFT and MP2 results, and (4) to establish a baseline for new methods designed for efficient quantum chemical calculations for large systems, such as the Effective Fragment Potential[4] (EFP) and Fragment Molecular Orbital[5] (FMO) approaches.

Our computational approach utilizes quantum chemical methods for prediction of ion cluster geometries, interaction energies, and vibrational spectra. Specific ion clusters of interest, which have been detected in vacuum electrospray ionization experiments,[6] include the following

clusters of the1-ethyl-3-methylimidazolium cation (abbreviated as [$Emim^+$] and shown in Figure 1a) and the *bis*(trifluoromethyl)sulfonylimide anion (denoted as [Im^-] and illustrated in Figure 1b): $[Emim^+]_j[Im^-]_k$; $1 \leq k \leq 3$, j=k or k±l. Geometry optimizations were performed using density functional theory (DFT) with the hybrid B3LYP functional[7] and the 6-311++G(d,p) basis set,[8] denoted as B3LYP/6-311++G(d,p). All structures were verified as local minima and harmonic vibrational frequencies were obtained via diagonalization of the mass-weighted matrix of energy second derivatives with respect to nuclear coordinates; i.e., the hessian matrix. Geometries, vibrational frequencies, and interaction energies were refined using second-order perturbation theory[9] (MP2, also known as MBPT(2)) with the 6-311++G(d,p) basis set[8], denoted as MP2/6-311++G(d,p). All computations were performed using the GAMESS quantum chemistry code.[10]

Since the potential energy surfaces of these systems tend to be rather "flat", it is necessary to use more stringent convergence criteria for geometry optimization of ion clusters in order to obtain reliable structural predictions. Consequently, geometry optimizations of these clusters, which consist of a systematic sequence of energy+gradient evaluations, generally require up to thousands of steps to converge. Therefore, significant computational resources are needed for these types of computations. For example, optimization of the structure of the $[Emim^+]_2[Im^-]_3$ ion cluster required approximately 3 million cpu hours on the Cray XT3 at the ERDC DSRC.

As a starting point, the structure of the [$Emim^+$][Im^-] ion pair was computed. At the B3LYP/6-311++G(d,p) level, three distinct local minima were found and are shown in Figure 2. The binding energies E_b are given in kJ/mol and indicate the energy required to separate the ions. The DFT binding energies for the three ion pairs are similar. In Figure 2a, the anion is located partially above the ring of the cation, suggestive of an attractive electrostatic interaction between the anion and the five-membered ring π electron density (located above and below the plane of the ring.) In contrast, the anion in Figures 2b and 2c is located along the side of the cation ring. The dominant interactions in 2b and 2c are hydrogen bonds, which are weak attractive electrostatic interactions between a hydrogen atom which carries a partial positive charge and another atom bearing a partial negative charge. In 2b and 2c, hydrogen bonding occurs between the hydrogen atoms on the cation and the oxygen atoms on the anion. Note that 2c has an additional hydrogen bond between the cation and the nitrogen atom in the anion. Charge neutralization does not occur in any of the three local minima.

The minima shown in Figure 2 were reoptimized at the MP2/6-311++G(d,p) level and are shown in Figure 3. Note that the binding energies are significantly larger relative to DFT. The most stable structure is shown in Figure 3a, in which the anion is located directly above the cation ring. The primary interaction in 3a appears to be between the nitrogen atom of the anion and the π density of the cation ring. In the structure shown in Figures 3b, the anion is partially located above the cation ring with one of the $-CF_3$ groups positioned over the π density of the ring. Finally, in the isomer shown in Figure 3c, the anion is located along the side of the cation ring and is similar to the DFT isomer shown in Figure 2c, indicative of hydrogen bonding interactions between the ions. As in the case of DFT, charge neutralization does not occur in any of the three minima.

The DFT predicted structure of the $[Emim^+]_2[Im^-]$ ion cluster is shown in Figure 4a. Not surprisingly, the cations are arranged on opposite sides of the anion in order to minimize the electrostatic repulsion between their positive charges. Note that the dominant interactions are

hydrogen bonds between the cations and the oxygen and nitrogen atoms of the anion with no interactions present between the anion and the π density of the ring cations, similar to the interactions seen in Figures 2b and 2c.

Figure 4b illustrates the MP2 predicted geometry of the $[Emim^+]_2[Im^-]$ ion cluster. As in the case of the DFT structure in Figure 4a, the cations are located on opposite sides of the anion. However, note that one of the cations is positioned to interact with the anion via its π electron density, whereas the other cation is located along the side of the cation ring so that its interactions with the anion are dominantly hydrogen bonding in nature. As in the case of the $[Emim^+][Im^-]$ ion pairs, the MP2 predicted binding energy (508 kJ/mol) is considerably larger than the DFT value (437 kJ/mol).

Figures 5a and 5b show the DFT and MP2 predicted structures of the $[Emim^+][Im^-]_2$ ion cluster. As expected, the cation is sandwiched between the anions in both structures. The DFT predicted geometry shows the presence of hydrogen bonding between the cation and anions, whereas the MP2 structure has the anions interacting with the π electron density of the cation ring. As in the previous clusters, the MP2 binding energy (519 kJ/mol) is larger than DFT (401 kJ/mol), and charge neutralization does not occur.

In summary, the structures, harmonic vibrational frequencies, binding energies, and internal thermal energy distributions of gas-phase ion clusters of the 1-ethyl-3-methylimidazolium *bis*(trifluoromethylsulfonyl)imide ionic liquid have been predicted using density functional theory (B3LYP/6-311++G(d,p)) and second order perturbation theory (MP2/6-311++G(d,p)). Comparisons between the DFT and MP2 results show that the latter generally favor interactions between the anion and the π electron density of the cation ring, whereas the DFT geometries tend to favor interionic hydrogen bonding. Furthermore, MP2 predicts significantly stronger interaction energies relative to DFT. Ongoing studies includes reoptimization of the DFT predicted structures of the larger $[Emim^+]_2[Im^-]_3$ and $[Emim^+]_3[Im^-]_2$ clusters at the MP2 level and refinement of the calculated binding energies using coupled cluster theoretical methods (e.g., coupled cluster single and double excitations with perturbative estimates of triples, CCSD(T)[11]). Future efforts will include similar studies of ion clusters obtained from the1-butyl-3-methylimidazolium dicynamide ionic liquid.

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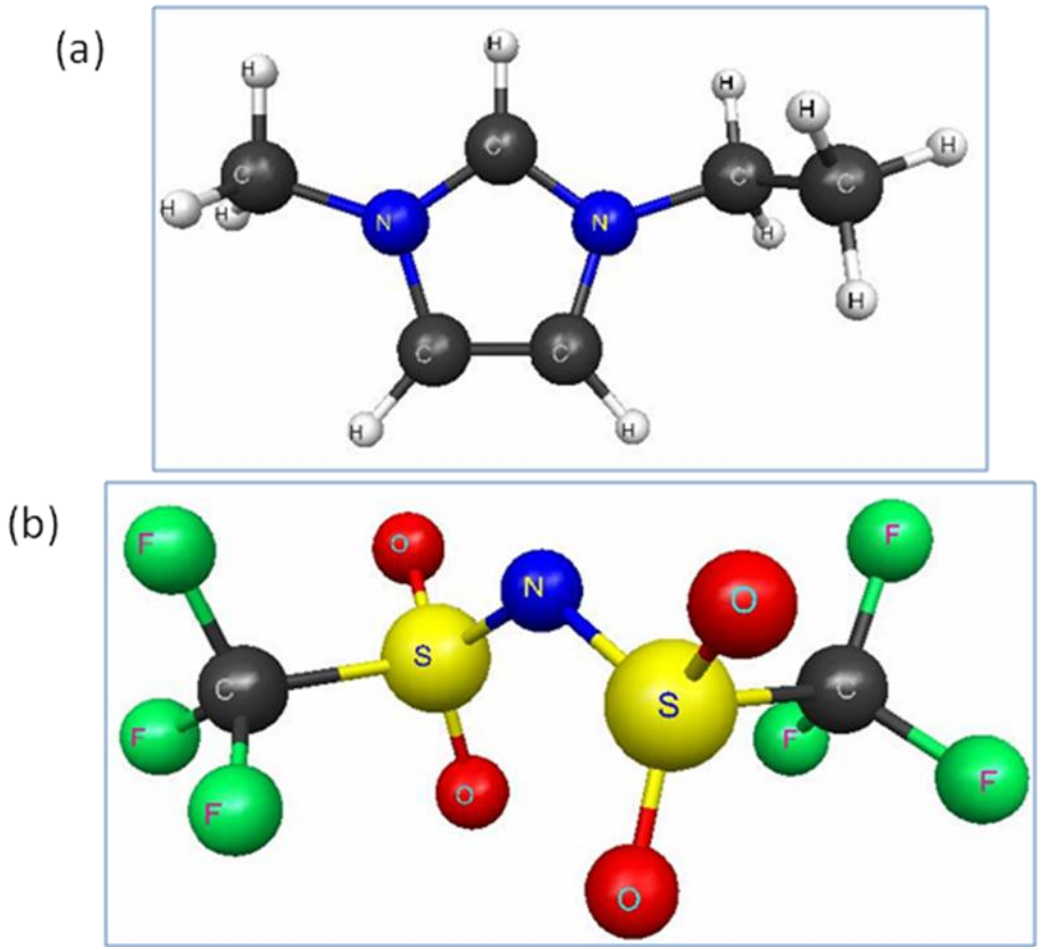

Figure 1. B3LYP/6-311++G(d,p) optimized structures of (a) the 1-ethyl-3-methylimidazolium cation and (b) the *bis*(trifluoromethyl)sulfonylimide anion. Hydrogen, carbon, nitrogen, oxygen, fluorine, and sulfur atoms are shown in white, black, blue, red, green, and yellow, respectively.

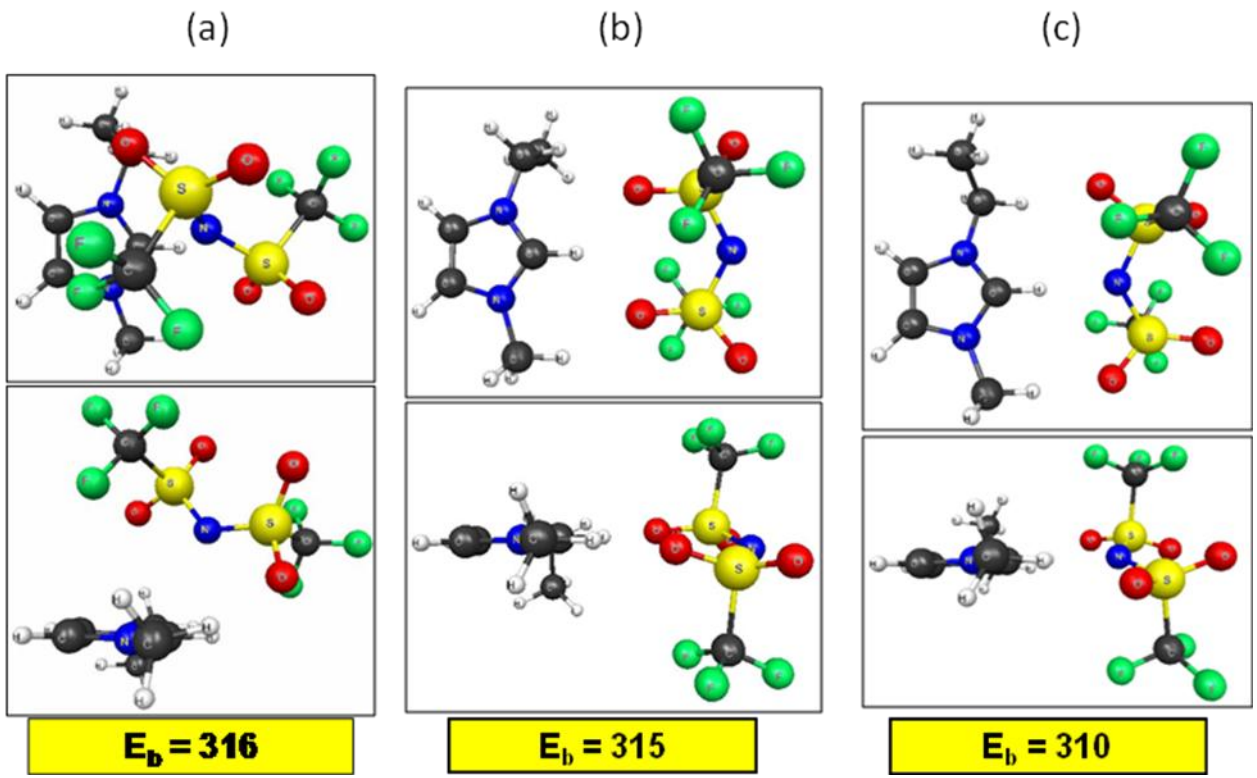

Figure 2. B3LYP/6-311++G(d,p) optimized structures of [Emim$^+$][Im$^-$] ion pairs. The binding energy E_b (in kJ/mol) is the energy required to separate the ions. Each panel shows two views of the same structure.

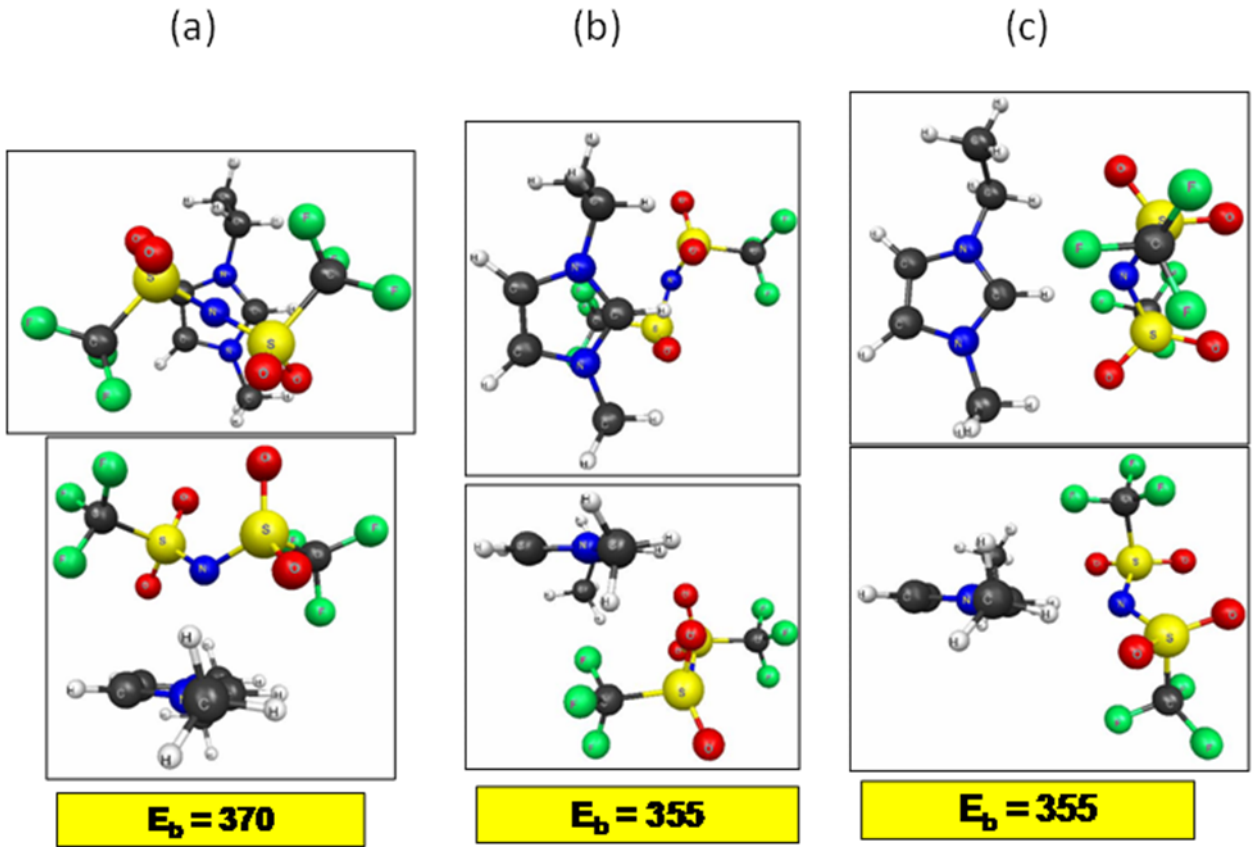

Figure 3. MP2/6-311++G(d,p) optimized structures of [Emim$^+$][Im$^-$] ion pairs. The binding energy E_b (in kJ/mol) is the energy required to separate the ions. Each panel shows two views of the same structure.

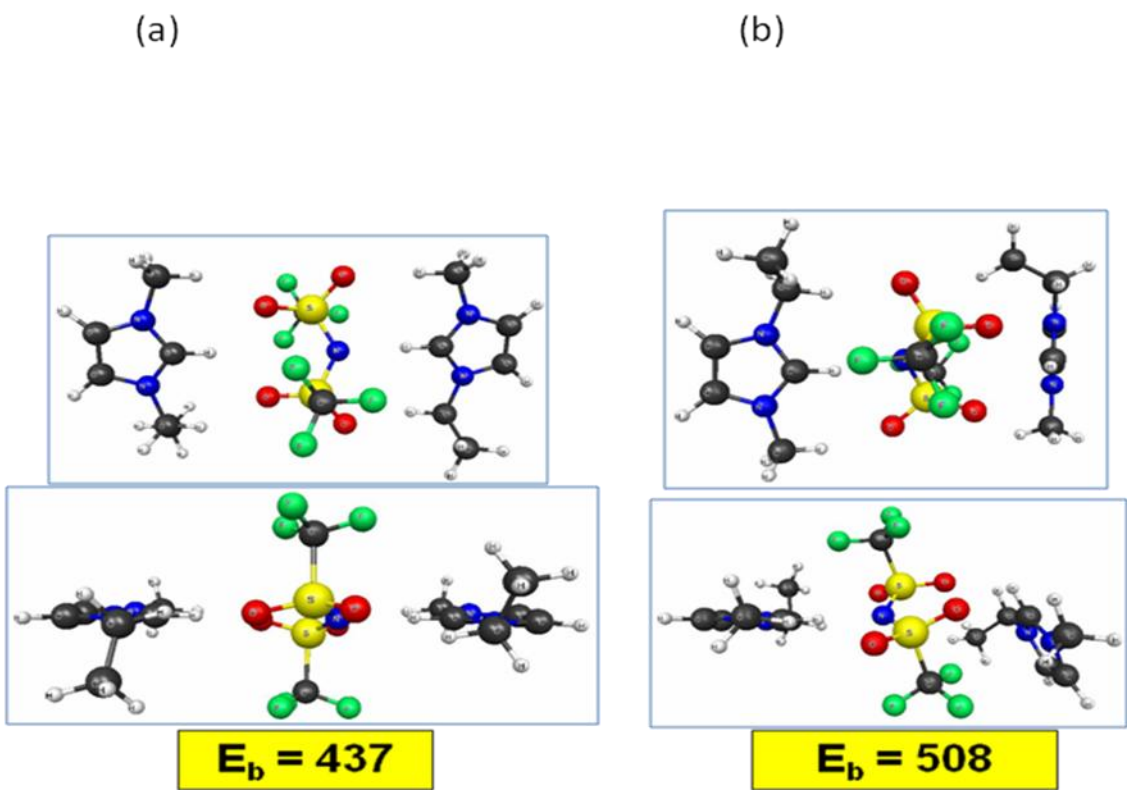

Figure 4. (a) B3LYP/6-311++G(d,p) and (b) MP2/6-311++G(d,p) optimized structures of the $[Emim^+]_2[Im^-]$ ion cluster. The binding energy E_b (in kJ/mol) is the energy required to separate the ions. Each panel shows two views of the same structure.

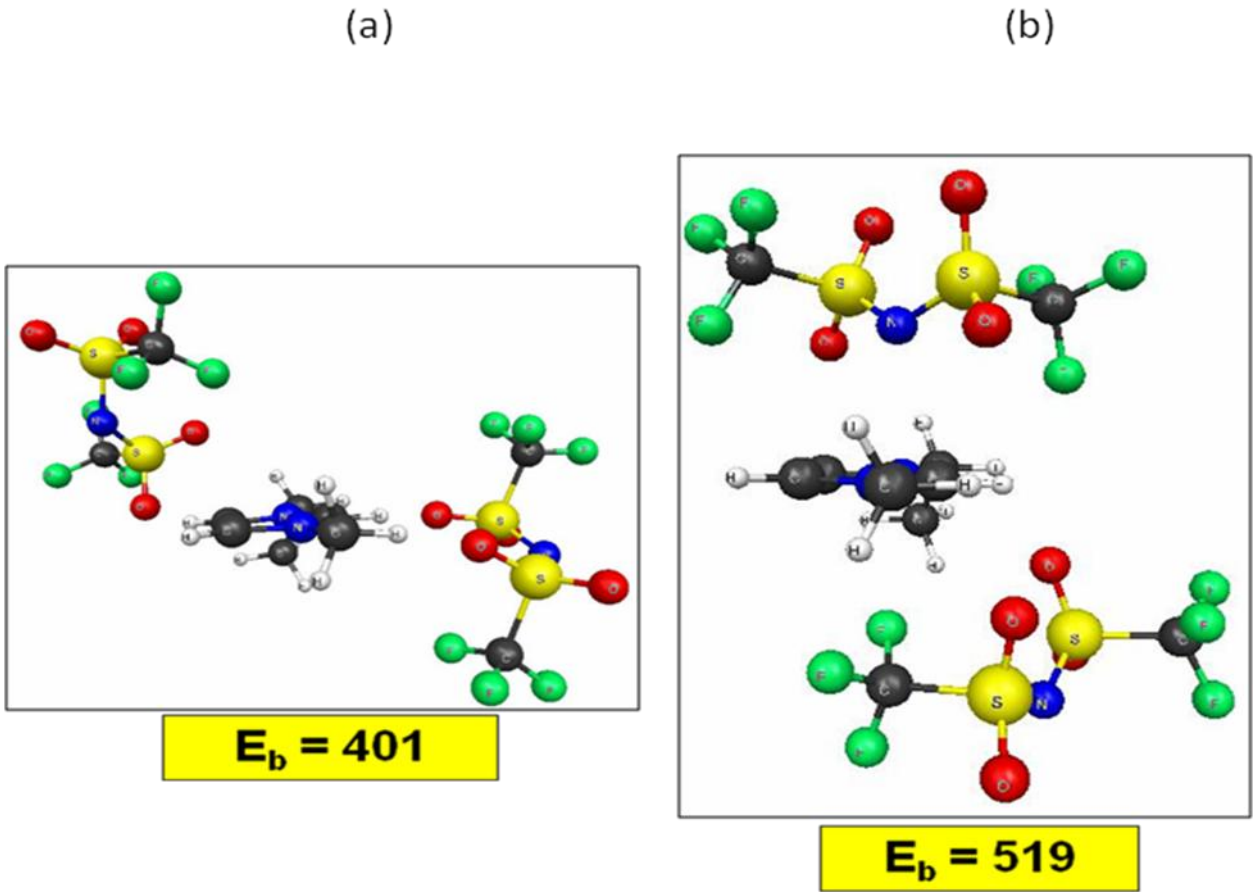

Figure 5. (a) B3LYP/6-311++G(d,p) and (b) MP2/6-311++G(d,p) optimized structures of the $[Emim^+][Im^-]_2$ ion cluster. The binding energy E_b (in kJ/mol) is the energy required to separate the ions.